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Spectroelectrochemical properties of homo- and heteroleptic ruthenium and osmium binuclear complexes

Halpin, Yvonne; Cleary, Laura; Cassidy, Lynda; Horne, Sabine; Dini, Danilo; Browne, Wesley R.; Vos, Johannes G.

Published in:
Dalton Transactions

DOI:
[10.1039/b823104d](https://doi.org/10.1039/b823104d)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2009

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Halpin, Y., Cleary, L., Cassidy, L., Horne, S., Dini, D., Browne, W. R., & Vos, J. G. (2009). Spectroelectrochemical properties of homo- and heteroleptic ruthenium and osmium binuclear complexes: intercomponent communication as a function of energy differences between HOMO levels of bridge and metal centres. *Dalton Transactions*, 25(21), 4146-4153. <https://doi.org/10.1039/b823104d>

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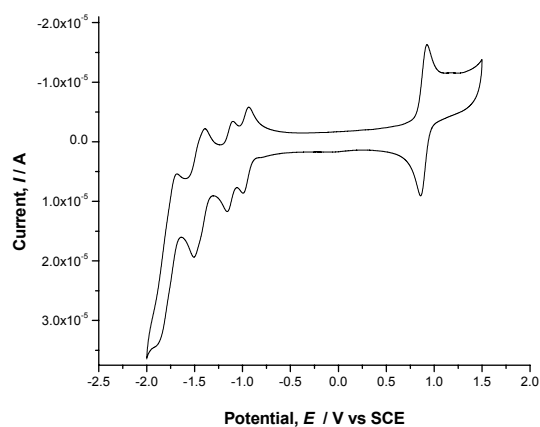


Fig. SI1. Cyclic voltammogram (CV) of **2** (1mM) in 0.1 M TBAPF₆ CH₃CN:CH₂Cl₂ (1:1) at 0.1 V s⁻¹.

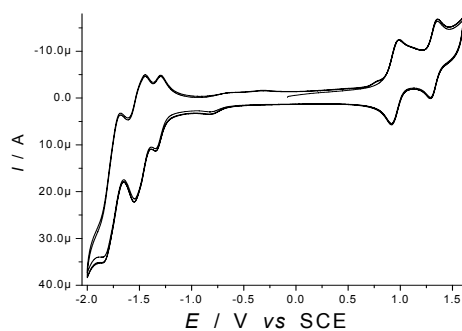


Fig. SI1. Cyclic voltammogram (CV) of **3** (1mM) in 0.1 M TBAPF₆ CH₃CN:CH₂Cl₂ (1:1) at 0.1 V s⁻¹.

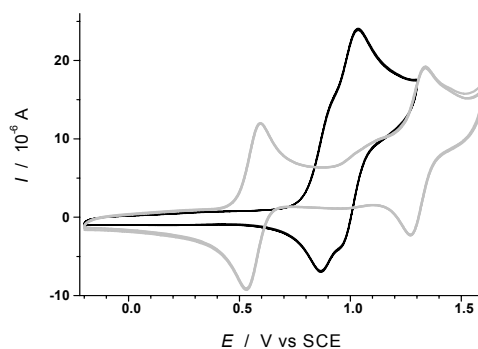


Fig. SI2. Cyclic voltammogram (CV) of $[(\text{bipy})_2\text{Ru}(\text{pytr-bipy})\text{Os}(\text{bipy})_2]^{3+}$ (**4**) (1 mM, black trace) and $[(\text{bipy})_2\text{Os}(\text{pytr-bipy})\text{Ru}(\text{bipy})_2]^{3+}$ (**5**) (1 mM, grey trace) in 0.1 M $\text{TBAPF}_6 \text{CH}_3\text{CN}:\text{CH}_2\text{Cl}_2$ (1:1) at 0.1 V s^{-1} .

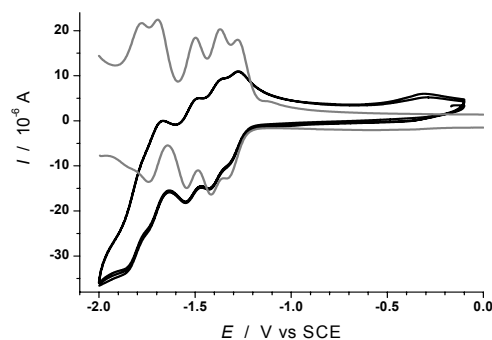


Fig. SI4. Cyclic (black trace) and differential pulse (grey trace) voltammograms of **5** (1mM) in 0.1 M $\text{TBAPF}_6 \text{CH}_3\text{CN}:\text{CH}_2\text{Cl}_2$ (1:1) at 0.1 V s^{-1} .

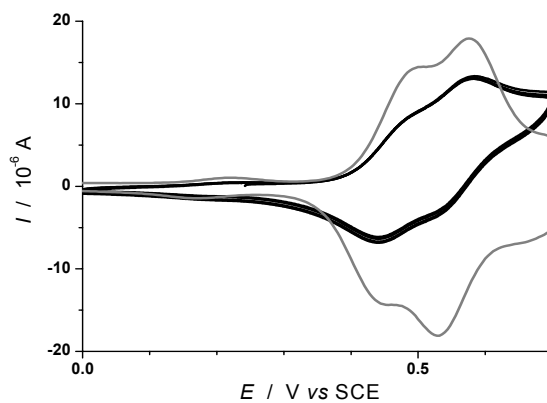


Fig. SI5. Cyclic (black line) and differential pulse (grey line) voltammograms of **6** (1mM) in 0.1 M $\text{TBAPF}_6 \text{CH}_3\text{CN}:\text{CH}_2\text{Cl}_2$ (1:1) at 0.1 V s^{-1} .

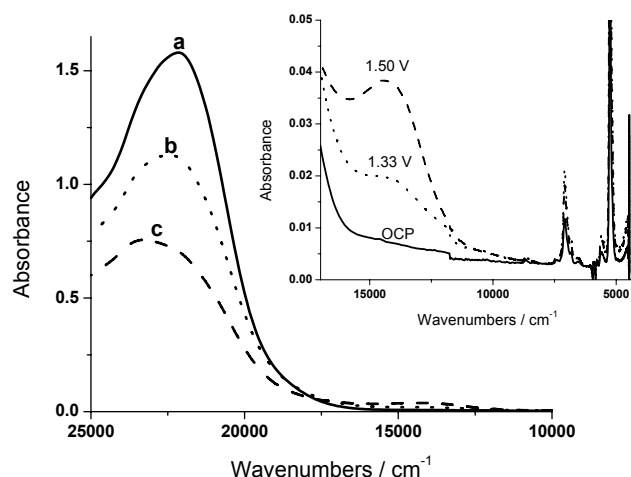


Fig. SI6. UV/Vis-NIR absorption spectra of $[(\text{bipy})_2\text{Ru}(\text{qpy})\text{Ru}(\text{bipy})_2]^{4+}$ (**1**) in 0.1 M TBAPF₆/CH₃CN at (a) $E = \text{OCP}$ (open circuit potential) (b) $E = 1.33 \text{ V}$ [Ru(III)-Ru(II)] and (c) $E = 1.50 \text{ V}$ [Ru(III)-Ru(III)]. vs SCE. Inset: expansion of NIR region.

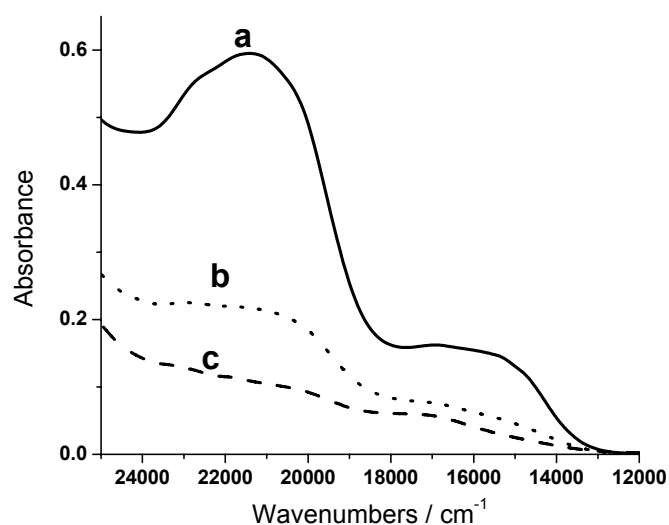


Fig. SI7. UV/Vis-NIR absorption spectra of $[(\text{bipy})_2\text{Os}(\text{qpy})\text{Os}(\text{bipy})_2]^{4+}$ (**2**) in 0.1 M TBAPF₆/CH₃CN at (a): $E = \text{OCP}$; (b) $E = 0.89 \text{ V}$ [Os(III)-Os(II)] and (c) $E = 1.20 \text{ V}$ [Os(III)-Os(III)] vs SCE.

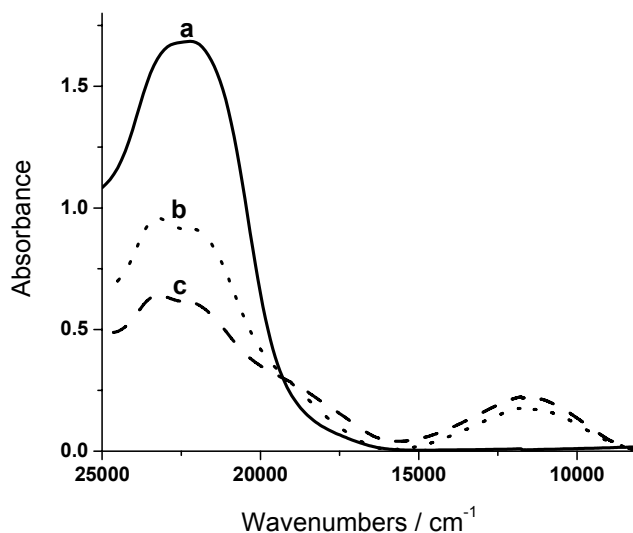


Fig. SI8. UV/Vis-NIR absorption spectra of $[(\text{bipy})_2\text{Ru}(\text{pytr-bipy})\text{Ru}(\text{bipy})_2]^{3+}$ (**3**) in 0.1 M TBAPF₆/CH₃CN at (a) $E = \text{OCP}$; (b) $E = 1.10 \text{ V}$ [Ru(III)-Ru(II)]; (c) $E = 1.40 \text{ V}$ [Ru(III)-Ru(III)] vs SCE.

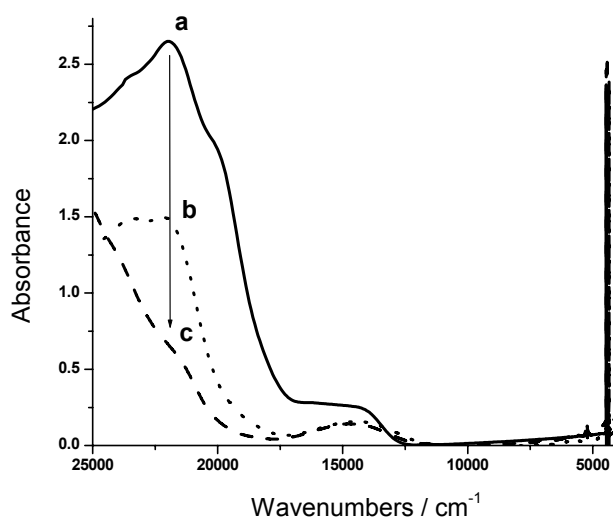


Fig. SI9. UV/Vis-NIR absorption spectra of $[(\text{bipy})_2\text{Os}(\text{pytr-bipy})\text{Ru}(\text{bipy})_2]^{3+}$ (**5**) in 0.1 M TBAPF₆/CH₃CN at (a) $E = \text{OCP}$, (b) $E = 0.90 \text{ V}$ [Os(III)-Ru(II)] and (c) $E = 1.50 \text{ V}$ [Os(III)-Ru(III)] vs SCE.